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Magnetic Susceptibilities of Solid Oxygen-Argon Mixtures

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The magnetic susceptibility in solid oxygen-argon mixtures has been obtained as a function of the temperature from 12 K to the melting point. In case of the 95% O_2–5% Ar system, the behavior of the magnetic susceptibility was similar to that of pure oxygen except for some dynamical effects caused by the addition of argon to the oxygen lattices. In the composition range between 92% and 66% O_2, the appearance of a novel phase, δ, was observed from the magnetic susceptibility measurements; its temperature and concentration dependence was discussed qualitatively on the basis of the crystal structure.

The magnetic susceptibility of solid oxygen was first measured from 2 K to its melting point by Kanda *et al.*[1] Since then, the magnetic properties of solid oxygen have been studied by various methods, such as crystallographic analysis,[2] optical-absorption measurements in relation to magnon excitation,[3] and electronic 'double' transitions.[4]

It has been clarified through these studies that there exists an antiferromagnetic spin ordering over a long range in the lowest-temperature α phase; in this sample the crystal structure is monoclinic and nearly closed-packed in both [001] and [$\bar{2}$01] planes. On the other hand, in the higher-temperature phases, β (23.8—43.8 K) and γ (43.8—54.4 K), the order is only short range because of the nearest-neighbor interactions.

In the present study, the results of magnetic susceptibility measurements of oxygen-argon mixtures with oxygen contents between 66% and 95% will be reported and the effects of the addition of diamagnetic argon atoms will be discussed.

Experimental

The magnetic susceptibitily measurements were carried out from 12 K to the melting point in each of the oxygen-argon mixtures by the Faraday method, as has previously been described.[5] The magnetic field was set at about 9×10^3 Gauss throughout the measurements. The field strength was calibrated by measuring the susceptibility of sucrose, the mass susceptibility of which was taken to be -0.566×10^{-6} emu/g.

The preperation method and the thermal history of the sample were as follows. Gaseous mixtures of oxygen and argon in various ratios containing 5—10 mg of oxygen were condensed into a small quartz tube cooled at the temperature of liquid helium, and then the tube was sealed off. The quartz ampoule (5 mm in diameter and 15 mm in length) was suspended by a Pyrex glass string from the arm of a Saltorius Electrono Microbalance, cooled to about 80 K, and kept at this temperature for more than ten minutes in order to liquefy and mix the gases. This liquid mixture was then solidified at about 50 K. After this treatment, it was cooled to 12 K within less than 15 min.

The temperature was measured with an Au : Co–Cu

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1) E. Kanda, T. Haseda, and A. Otsubo, *Physica*, **20**, 131 (1954).

2) M. F. Collins, *Proc. Phys. Soc.* (London), **89**, 415 (1966). C. S. Barrett, L. Meyer, and J. Wasserman, J. Chem. Phys., **47**, 592 (1967).

3) T. G. Blocker, M. A. Kinch, and F. G. West, *Phys. Rev. Lett.*, **22**, 853 (1969). E. J. Wachtel and R. G. Wheler, *ibid.*, **24**, 233 (1970).

4) Yu. G. Litvinenko, V. V. Eremenko, and T. I. Garber *Phys. Stat. Sol.*, **30**, 49 (1968).

5) N. Ohigashi and H. Inokuchi, This Bulletin, **42**, 1212 (1969).

thermocouple placed below the ampoule. The temperature of the sample was calibrated by the phase-transition temperatures of pure solid oxygen and also by measuring several times the susceptibilities of the paramagnetic salts whose suscepitibilities are known, Mohr's salt ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$) and Tutton's salt ($Mn(NH_4)_2(SO_4)_2 \cdot 6H_2O$), under the same conditions.

Results and Discussion

Figure 1 shows the temperature dependence of the magnetic susceptibility at each oxygen molar ratio, corrected for the diamagnetism of the argon and the quartz ampoule.

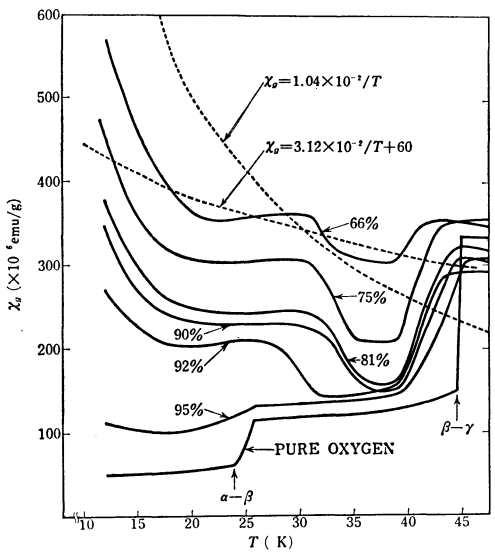

Fig. 1. The magnetic susceptibility of solid oxygen-argon systems.

In case of the 95% O_2, the behavior of the magnetic susceptibility was very similar to that of pure oxygen. This shows that the antiferromagnetic properties characteristic of each crystalline phase, α, β, and γ, of solid oxygen are not so much affected at these low concentrations of argon.

From the viewpoint of the dynamics of crystallization, however, this solid was found to behave differently from pure oxygen. The transformation temperatures from β to γ are lowered to about 40 K. The transformation process was also observed to be less discontinuous; an abrupt change in the susceptibility at each transition temperature, as in pure solid oxygen, was not observed in this mixture even at the slowest of temperature increases (1 °C/min), which was controlled by changing the vacuum in the Dewar vessel. Because of this experimental design, the susceptibility did not reach equilibrium during the transformation. These dynamical effects resulting from the addition of argon to the oxygen lattice have been previously observed in a determination of the oxygen-argon system by Barrett *et al.*,[6] and also through the measurement of the specific heat.[7]

On the other hand, with a further increase in the argon content, the magnetic susceptibilities showed some behavior very different from that of pure oxygen and the 95% O_2 mixture. They are consistent with an interesting phenomenon discovered by Barrett,[5] namely, that a novel homogeneous phase, 'δ', different from the phase of pure oxygen and pure argon, exists in the composition range between 55 and 80% O_2, while the monoclinic phase disappears. Furthermore, the upper limit of oxygen content at which the δ phase appears can be extended to 90% when the mixture is cooled from the γ phase down to the temperature of liquid hydrogen within less than an hour.

The stable-temperature region of this phase was estimated from the decrease in the susceptibility to be below 30—31 K for the 90%, 81%, 75%, and 66% oxygen mixture. In the case of the 92% O_2 and 8% Ar samples, a similar decrease in susceptibility was observed, but at a slightly lower temperature, about 26 K. These transformation temperatures do not agree in detail with those of the phase diagram.[6] According to this, the δ phase containing 80—90% O_2 is transformed to the β phase via a two-phase $\delta+\beta$ region at temperatures between 25 and 29 K, and that of 66—80% is transformed to the hexagonal closed-packed phase of argon + the β phase via the $\delta+\beta$ region at 29 K. This discrepancy may arise from the fact that the magnetic susceptibility measurements can not give such a sensitive indication of these complex transformation processes as X-ray diffraction analysis.

The temperature and concentration dependence of the susceptibility in the δ-phase region can be interpreted on the basis of the crystal structure. A possible structure of the δ phase was also determined by Barrett.[8] According to their work, unit cell has a body-centered cubic lattice with $a=13.23\pm0.02$ Å and $Z=64$, which is a super lattice of the γ structure

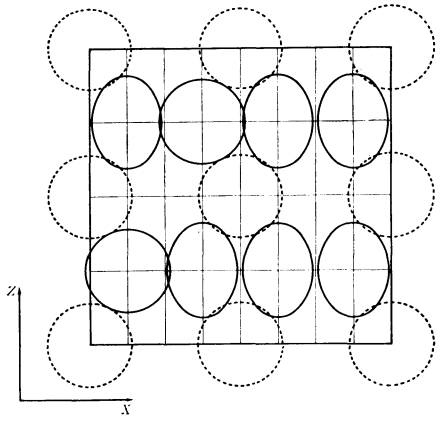

Fig. 2. The [010] plane of unit cell of the δ structure belonging to the space group I_{2_13}. The solid and dotted circles represent argon atoms with a diameter of 3.75 Å. The ellipses represent oxygen molecules with a major axis of 3.18Å.[10] The tilting of the molecular axis is postulated to be in this plane. The corner's argon represented by a dotted circle is displaced by 0.005, 0.005, 0.005 from each position along the threefold axis.

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7) E. L. Pace and R. L. Bivens, *ibid.*, **53**, 748 (1970).

8) C. S. Barrett, T. H. Jordan, and L. Meyer, *ibid.*, **51**, 2941 (1969).

of pure oxygen, with $a=6.83\pm0.05$ Å and $Z=8$. The position of the argon atoms in the δ structure has not been exactly determined, but some plausible models have been suggested. One of them is illustrated in Fig. 2. In this model, the argon and oxygen molecules are placed in a periodic sequence as; $\cdots Ar,O_2,O_2,O_2\cdots$ in the rows across the middle of the cube faces denoted 'γ rows.' The distance between the oxygen molecules in a γ row is 3.31 Å, which is equal to the nearest-neighbor distance in β-O_2 and about 0.1 Å shorter than in γ-O_2. Therefore, we can expect that there exists a fairly strong antiferromagnetic exchange interaction between these three oxygen molecules $(O_2)_3$ in a γ row. Consequently, the total spin moment of this trimer of the form $(O_2)_3$ decreases and becomes one in the antiferromagnetic short-range ordered state.

The paramagnetic increase below about 20 K is dependent on the argon content and seems to obey a Curie-Wiess law. A qualitative interpretation can be given in terms of weak antiferromagnetic interactions between the corner or the body-center's oxygens and the trimer in a γ row. The exchange interaction for these oxygen molecules, separated by about 3.8 Å, estimated to be equal to or less than 2 K from the 'statistical' Weiss temperature obtained for oxygens dispersed into the f.c.c. lattice of argon.[9] If the argon ratio is increased, some of the sixteen oxygen molecules at the corner and body-center's sites are successively replaced by argon, that is, 0 for 81% O_2, 4 for 75% O_2 and 10 for 66% O_2, so that the exchange interaction is weakened. Furthermore, as the neighboring trimers are separated by more than 4.1 Å, the magnetic susceptibility increases, obeying a Curie-Weiss law with a nearly zero Weiss temperature and also a smaller total spin moment. This is represented in the limiting form, $\chi(\text{emu/g})=C'/T+\theta$, where θ is the Weiss temperature and where C' equals 1.043×10^4, that is, the value of 1/3 of 3.128×10^4 for a free oxygen molecule. A quantitative treatment, however, was not attempted because it was not possible to estimate the contributions of residual phases, such as the α and β phases of solid oxygen, and of oxygens randomly dispersed in the segregated argon matrix.

Some interesting phenomena due to δ-phase transformation have also been observed from magnetic susceptibility measurements in solid oxygen-fluorine systems. These results will be reported elsewhere.

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10) R. F. W. Bader, W. H. Henneker, and P. E. Cade, *J. Chem. Phys.*, **46**, 3341 (1967).